CAPÍTULO 5

EXTRAÇÃO POR SOLVENTE DE ÁCIDO CÍTRICO EM UMA COLUNA MECANICAMENTE AGITADA

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RESUMO: O presente trabalho avalia a extração contínua de ácido cítrico em uma coluna mecanicamente agitada (tipo Kühni, 60 mm de diâmetro interno) com 20 estágios. A fase aquosa consistia de uma solução sintética de ácido cítrico (pH = 1.5) com concentração típica dos mostos fermentados industriais (10% m/v). O solvente utilizado era composto pelo extratante Alamine® 336 (30% m/v), uma amina terciária; o modificador Exxal™ 13 álcool tridecílico (10% m/v); e o diluente Escaid™ 110. Nos experimentos em escala piloto, foram investigadas diferentes razões de taxas volumétricas entre as fases orgânica e a aquosa (F_d/F_c of 1/3, 2/2, e 3/1). Assim, foram obtidos os perfis de concentração para ambas fases ao longo da coluna, e o hold up e a velocidade de deslizamento foram calculados para a operação em regime estacionário. A melhor

condição de extração foi obtida para a condição F_d/F_c of 2/2, por causa da alta extração (85%) e alta concentração do extrato, 9,1 % m/m de ácido cítrico.
PALAVRAS-CHAVE: ácido cítrico; coluna mecanicamente agitada; extração líquido-líquido

SOLVENT EXTRACTION OF CITRIC ACID IN A MECHANICALLY AGITATED COLUMN

ABSTRACT: The present work evaluated the continuous solvent extraction of citric acid in a mechanically agitated column (Kühni type, 60 mm internal diameter) with 20 stages. The aqueous phase was a synthetic solution of citric acid (pH = 1.5) with the typical concentration of industrial fermented musts (10% w/v). The solvent used was composed of the extractant Alamine® 336 (30% w/v), a tertiary amine; the modifier Exxal™ 13 tridecyl alcohol (10% w/v); and the diluent Escaid™ 110. Through pilot scale experiments, different volumetric flow rates ratios between the organic and aqueous phases (F_d/F_c of 1/3, 2/2, and 3/1) were investigated. Therefore, concentration profiles in both phases along the column, operating in steady state, were obtained and hold up and slip velocity were calculated. The better extraction condition was to F_d/F_c of 2/2, because of the high extraction (85%) and high extract concentration 9.1 % w/w of citric acid.
KEYWORDS: citric acid; mechanically agitated column; solvent extraction

INTRODUCTION

Citric acid is an important chemical produced worldwide; its annual output can reach 1.4 tons per year, and its demand is continually growing from 3.5 to 4.0 % per year. Some of the main world manufactures are Shandong Juxian Hongle Citric Acid Co. Ltd., Cargill and Tate & Lyle. The major citric acid production is through the fermentation of musts using yeasts. The filtered must after fermentation presents an acid concentration between 8 and 15% w/v, and a pH value among 1.6 and 2.6 (Garibay *et al.*, 1993). A key operation in the production process is the citric acid purification from the fermented must.

One of the existing purification methods is the solvent extraction. Although this method is already applied industrially, the access to operational parameters and stream compositions is quite restricted. According to Pazouki and Panda (1998), among the several existing patents on this method, only those that use tertiary amines as extractant and do the striping with hot water presents feasible conditions to industrial application.

Using extraction columns to promote the separation of organic and inorganic species in different media is becoming increasingly common in industrial liquid-liquid extraction operations. The agitated columns are the most suitable for applications that require a more effective contact between the phases, providing higher interfacial areas and a better homogenization. The advancements in extraction columns have led to a growing application of columns in chemical, pharmaceutical, petrochemical, and hydrometallurgical industries.

The evaluation of the flow and mass transfer conditions inside the column is fundamental for industrial plant design and operational conditions establishment. This can

be done using data from pilot plants. The hydrodynamic behavior of a liquid-liquid system involves studying the phenomena of phases flow throughout the column. Several parameters are used to describe it, such as the hold up (), the slip velocity (). The hold up is defined by the ratio between the volume of dispersed phases and the total volume of the dispersion. This parameter measures the fraction of dispersed phases present in the column. The slip velocity is the velocity of the dispersed phase in relation to the continuous phase, in this case, of the organic phase in relation to the aqueous phase (Laddha and Degaleesan, 1991; Míšek, 1994).

The ratio between the flow rates of dispersed and continuous phase (F_d/F_c) has a direct effect on the column efficiency. Low ratios values imply in a small fraction of dispersed phase, which means having a small interfacial area for chemical reaction and mass transfer. High values are also unsuitable, because it can cause other effects, such as flooding.

In the light of the above, the present work aimed the extraction of citric acid using Alamine® 336 (a mixture of trialkylamine - TAA) in a pilot unit. The acid was extracted from a synthetic solution containing 10% w/v of citric acid (pH=1.5), a typical concentration of fermented musts. It was studied the hydrodynamics of this system in a mechanically agitated, Kühni type column.

EXPERIMENTAL

Materials

The reagents, used as supplied by the manufacturers, were: anhydrous citric acid (> 99.5% purity – Vetec); Alamine® 336, extractant (> 95 % tertiary amine – BASF); Escaid™ 110 (diluent) and Exxal™ 13 tridecyl alcohol (modifier), both from ExxonMobil.

The aqueous phase was prepared just before each experiment; it was a synthetic solution of citric acid with concentration of 10% w/v (100 $g.L^{-1}$) and pH of 1.5.

The organic phase was composed of the extractant Alamine® 336 (37.5% w/w), a trialkylamine (TAA); the modifier Exxal™ 13 tridecyl alcohol 12.5% w/w; and the diluent Escaid™ 110. This was determined in previous bench scale experiments. The Eq. (1) shows the reaction between citric acid and TAA. In this equation, the subscripts *aq* and *org* refer to the aqueous and organic phases, respectively; n refers to the number of amine molecules required to reacts with one citric acid molecule (Bízek *et al.*, 1992).

$$(H_3Cit)_{\mathrm{aq}} + n(TAA)_{\mathrm{org}} \rightleftharpoons ((TOAH)_n \cdot H_{3-n}Cit)_{\mathrm{org}} \qquad \mathrm{n} = 1, 2, 3 \qquad (1)$$

Methods

In the experiments, it was used a mechanically agitated column with two modules of 10 stages each (20 stages in total). Each module had a length of 350 mm, an internal diameter of 60 mm, and an external diameter of 100 mm. Each stage was separated by perforated plates (Figure 1), with 30% of free area to the phases flow. In addition, the column had a top and a bottom settler, with 240 and 255 mm, respectively. The stirring, kept at 300 rpm, were done by a central axis, in which turbine type impellers were coupled. The inlet of aqueous phase was located in the top of the column, while the organic phase was feed in the bottom.

For the equipment startup, the column was initially filled with the aqueous phase (continuous phase). Then, the flow of this phase was interrupted, the stirring was turned on and the pumping of organic phase (dispersed phase) was initiated. When the organic phase reached the settler outlet, the aqueous phase pump was started. The volumetric flow rates ratios (F_d/F_c), between the dispersed (F_d) and continuous phase (F_c), of 1/3, 2/2, and 3/1 were studied for a total flow rate of 4 $L.h^{-1}$. Table 1 shows all the parameters used in the experiments.

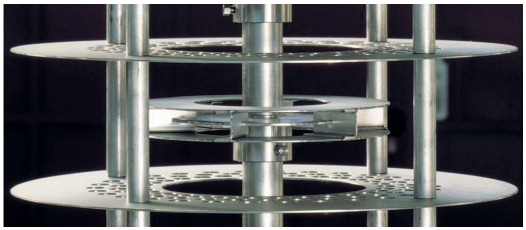

Figure 1 – Column internals used in the tests.

Fonte: KONZEN (2013)

Investigated Parameters	**Evaluated Levels**
Volumetric flow rate of each phase / ($L.h^{-1}$)	1, 2, 3
Volumetric flow rate ratio (F_d/F_c)	1/3; 2/2; 3/1
Fixed Parameters	**Levels**
Temperature / (°C)	28 ± 2
Stirring speed / (rpm)	300
Total flow rate / ($L.h^{-1}$)	4
Total time of the experiment / (h)	5 – 5.5

Table 1 - Column experiments: investigated and fixed parameters and their respective levels.

During this time, samples of 20 mL were collected in the stages 3, 7, 14, 18, in the top settler (organic phase - extract), and in the bottom settler (aqueous phase - raffinate). These samples were kept still for the phase separation (around 5 min) and the volume of each phase was measured to calculate the local dispersed phase hold up and the slip velocity. The total hold up was calculated as the mean of the local hold up values. For each condition of F_d/F_c ratio studied, the slip velocity ($\bar{v}_s$) of the dispersed phase in relation to the continuous phase was calculated using Eqs. (2) and (3) (Konzen, 2013).

$$\bar{v}_s = \frac{1}{C_R}\left(\frac{U_d}{\phi} + \frac{U_c}{1-\phi}\right) = \frac{1}{C_R}\left(\frac{\frac{F_d}{A_s}}{\phi} + \frac{\frac{F_c}{A_s}}{1-\phi}\right) \quad (2)$$

$$C_R = 0{,}75 S_\phi + 0{,}25 \quad (3)$$

In these equations, C_R is the constriction factor; S_ϕ is the fraction corresponding to the free area of the contactor section area in this case, 0.30; A_s is the column section area, equals to $2{,}83 \times 10^{-3}$ m^2. The subscripts *d* and c refer to the dispersed and continuous phases, respectively.

The acid concentrations in the aqueous phase before and after the extraction (raffinate), as well as in the organic phase after the extraction (extract) were measured by a complexometric titration with copper ions, using murexide as indicator (Konzen, 2013).

RESULTS AND DISCUSSION

Concentration Profiles

The Figure 2 shows the citric acid concentration profiles in the aqueous (continuous) and organic (dispersed) phases. The point prior to stage 1 refers to the input of citric acid solution (aqueous phase) and organic phase output (extract), which occurs in the top of the column. The point prior to stage 20 refers to the input of solvent feed and output of aqueous phase (raffinate), in the bottom of the column.

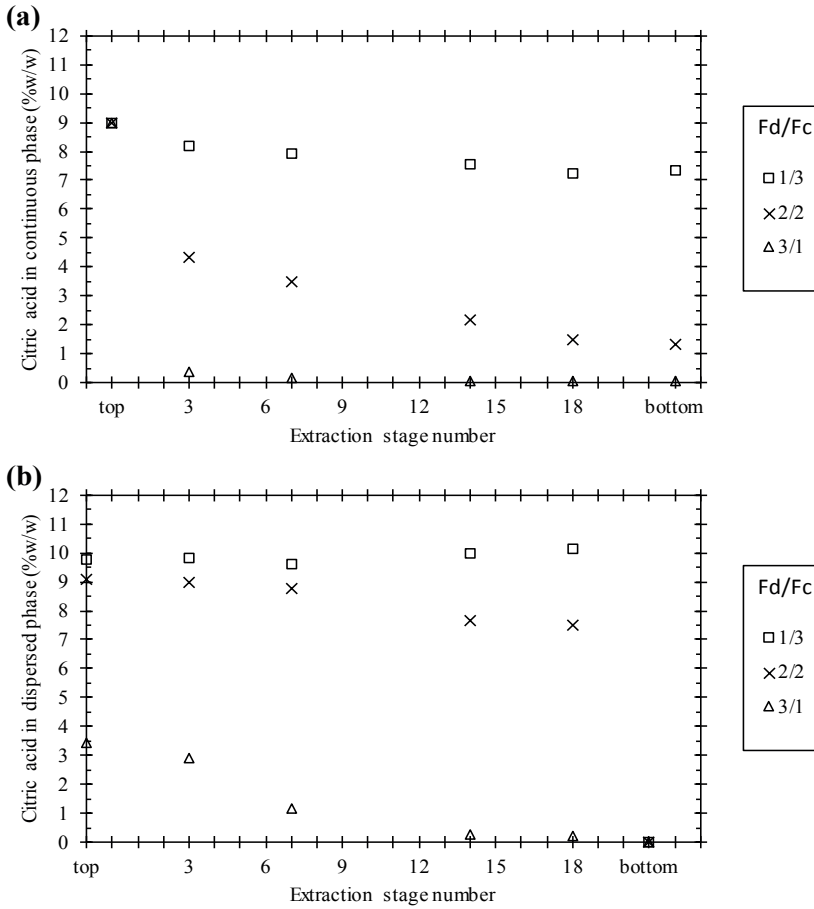

Figure 2 - (a) Aqueous phase and (b) organic phase concentration profiles throughout the column for different flow rate ratios Fd/Fc.

From Figure 2, it can be seen that the lowest extraction was obtained for the F_d/F_c ratio of 1/3. In this condition, the citric acid extraction percentage was 15%, and no large variation of the acid concentration in the aqueous phase was observed along the column. The raffinate and extract obtained have 7.3 and 9.7% w/w of citric acid, respectively. The reason for the low extraction was that the small amount of organic phase fed, in relation to the aqueous phase, was insufficient to extract the citric acid. Thus, right on the first stages, the organic phase became saturated and the raffinates remains concentrated in citric acid.

For the F_d/F_c ratio of 2/2, 85% of the citric acid fed was extracted. The raffinate and extract obtained had 1.3 and 9.1 % w/w of citric acid, respectively. For the F_d/F_c ratio of 3/1, an extraction of 99% was obtained, producing a raffinate with only 0.1% w/w of citric acid. In this condition, the acid was almost completely extracted in the first stages, because of the large amount of organic phase fed in relation to the aqueous phase. For this reason, the organic phase is obtained with much lower acid concentrations (3.4 % w/w).

Hydrodynamics

Figure 3 shows the local dispersed phase hold up values for the extraction stages sampled for the different flow rate ratios (Fd/Fc) investigated. The hold up tends to increase from the top to the bottom of the column mainly because the pressure caused by the liquid column height. It's not observed in stage 18, because this stage was close to the organic phase inlet. The dispersed phase hold up along the column can be affected by the variations in the dispersed phase droplet size caused by its breakage and coalescence during phase contact, as well as changes in physicochemical properties due to the acid extraction along the column (Konzen, 2013). Gomes *et al.* (2004) found an increase in the hold up value at the bottom of the column.

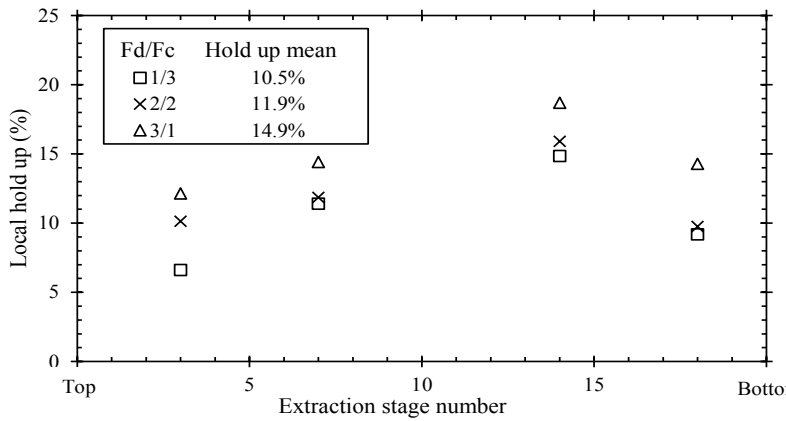

Figure 3 - Local dispersed phase hold up for each column stage and mean dispersed phase hold up for different Fd/Fc ratios

In addition, it can be observed that for a same stage, the local hold up increases for higher F_d/F_c ratios, i.e., when more dispersed phase is fed, as it was expected. The mean dispersed phase hold up (Figure 3) was calculated from the local hold up values for each flow rate ratio. It was found values of 10.5, 11.9, and 14.9% for the F_d/F_c ratios of 1/3, 2/2, and 3/1, respectively, increasing with the proportion dispersed phase feed.

Using the local dispersed phase hold up values and the Eqs. (2) and (3), the slip velocities ($\bar{v}_s$) were calculated (Figure 4).

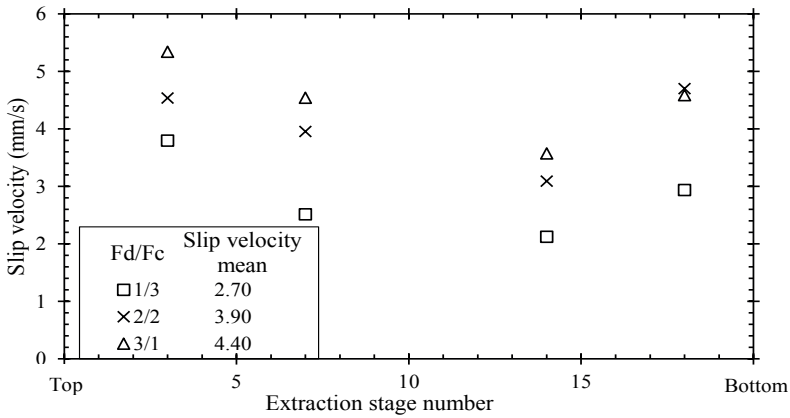

Figure 4 - Slip velocities for different Fd/Fc ratios investigated.

Regardless the extraction stage, the increase in the dispersed phase flow rate led to an increase in the slip velocity. The increase in both phases contributes to the increase in slip velocity, but as the dispersed phase hold up was much smaller than the continuous phase hold up, the effect of its variations with F_d are much significant than the effect of its variations with F_c. For each F_d/F_c ratio investigated, the slip velocities ($\bar{v}_s$) increased as the dispersed phase droplets ascended in the column, as the local dispersed phase hold up become smaller. The stage 18 suffers a variation in the flux caused by the feed of organic phase in the bottom of the column, so the results are less accurate in this stage. The mean slip velocity was calculated using the mean hold up values as a function of the F_d/F_c ratio. It was found values of 2.7, 3.9, and 4.4 mm.s^{-1} for the F_d/F_c ratios of 1/3, 2/2, and 3/1, respectively. The values obtained agree with the results discussed above.

CONCLUSIONS

In this work, it was evaluated the citric acid solvent extraction from synthetic solutions. Continuous extraction experiments were done in a mechanically agitated column of Kühni type. The main conclusions were:

- Increasing the volumetric flow rate of the dispersed phase (F_d), while keeping the total flow rate constant (F_t = 4 L.h^{-1}), has increased the dispersed phase hold up and the slip velocity ($\bar{v}_s$);
- The dispersed phase hold up is lower and the slip velocity is higher when the droplets rise along the column;
- For the same total flow rate (F_t), higher F_d/F_c ratios provided higher extraction percentages by increasing the extraction capacity, but the extract concentration reduces.
- The better condition was F_d/F_c = 2/2, that showed 85% of extraction, raffinate and extract with 1.3 and 9.1 % w/w of citric acid, respectively, ϕ = 11.9% and $\bar{v}_s$ = 3.90 mm.s^{-1}.

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